

PROCESS FACILITATING THE REGENERATION OF A CATALYST  
BASED ON A ZEOLITE USED IN AN ACYLATION REACTION.

CATALYST AND USE.

The present invention relates to a process  
5 facilitating the regeneration of a catalyst based on a  
zeolite, employed in an acylation reaction.

Another subject of the invention is a process  
for acylation of an aromatic ether, comprising, in a  
preferred alternative form, an additional stage of  
10 regeneration of the catalyst.

More particularly, the invention relates to a  
process for acylation in the position para to the  
alkoxy group carried by the aromatic nucleus.

The invention applies especially to the  
15 preparation of alkoxyaromatic alkyl ketones.

Conventional processes for acylation of  
aromatic compounds, especially of phenol ethers, make  
use, as acylating reactant, of a carboxylic acid or of  
one of its derivatives such as acid halide, ester or  
20 anhydride.

The reaction is generally conducted in the  
presence of a catalyst of the Lewis acid type (for  
example  $\text{AlCl}_3$ ) or of the Brönsted acid type ( $\text{H}_2\text{SO}_4$ , HF,  
and the like).

25 The use of zeolites as acylation catalysts  
has been proposed for som ten years.

Thus, the vapour phase reaction of an  
aromatic compound (veratrole) with a carboxylic acid

derivative in the presence of a zeolite in H form, such as mordenite, faujasite and ZSM-5, was described in EP-A-0279322.

US-A 4 960 943 also describes a process of  
5 acylation especially of anisole, in the presence of zeolites which have a pore size of at least 5 angstroms and which correspond to the following formula:

$M_{m/z} [mME^1O_2 \cdot nMe^2O_2] \cdot qH_2O$  in which M is an exchangeable cation, z is the valency of the cation and  $Me^1$  and  $Me^2$  denote the elements of the anionic lattice, n/m is a number between 1-3000, preferably 1-2000 and q denotes the adsorbed water.

The development of zeolites on an industrial scale is limited by the fact that zeolites are  
15 deactivated relatively quickly. In fact, the deactivation is doubtless attributed to poisoning of the catalyst by the heavy organic products formed during the reaction, which causes a lowering in the degree of conversion of the starting substrate, thus  
20 resulting in a drop of output efficiency.

The problem of reactivation of the catalyst then arises, which often involves a tedious regeneration procedure at high temperature (temperature above or equal to 500°C) requiring specific equipment.

25 The aim of the invention is to provide a process allowing the abovementioned disadvantages to be avoided.

The subject of the present invention is

precisely a process facilitating the regeneration of a zeolite-based catalyst employed in an acylation reaction, characterized in that the zeolite is modified by addition of an effective quantity of at least one 5 metallic element M chosen from the elements of group 8 of the Periodic Classification of the elements.

It has been found that the fact of doping the zeolite with a transition element of group 8 improves the regeneration of the catalyst, which can be carried 10 out, preferably, by simple oxidation with air at a temperature which is not particularly high.

In a preferred alternative form of the invention the process consists in choosing from the metals of group 8, more particularly those of the 15 platinum group.

"The platinum group" commonly denotes the group of the following six metals: ruthenium, rhodium, palladium, osmium, iridium and platinum.

It was found, unexpectedly, that the fact of 20 modifying the zeolite with an element of the platinum group, symbolized by  $M_1$ , resulted not only in an easier regeneration of the catalyst, but also enabled a good reaction yield and an excellent selectivity of the reaction to be obtained in the reaction of acylation of 25 an aromatic ether.

The zeolites thus modified are outstanding catalysts of acylation of an aromatic ether. The invention therefore also lies in a process for

acylation of an aromatic ether, preferably followed by a stage of regeneration of the catalyst.

According to a preferred alternative form of the process of the invention the acylation of the aromatic ether is first of all performed by reacting it with an acylating agent in the presence of an effective quantity of a zeolite modified with at least one element  $M_1$  of the platinum group, as defined, and then, after reaction, the regeneration of the catalyst is carried out by heat-treating it with a gas containing molecular oxygen.

This preferential embodiment of the process of the invention not only makes it possible to have good performance in respect of the acylation reaction but it is also possible to regenerate the catalyst very easily.

In accordance with the process of the invention the zeolite employed as catalyst in an acylation reaction is modified with a metallic element chosen from the elements of group 8 of the Periodic Classification of the elements.

For the definition of the elements reference is made below to the Periodic Classification of the elements as published in the Bulletin de la Société Chimique de France, No. 1 (1966).

Those involved are more particularly iron, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum.

A mixture of the said elements may also be employed.

Palladium or platinum may be mentioned as metallic elements which are preferably used.

5 The content of metallic element M in the zeolite is generally such that the percentage by weight of the metal relative to the zeolite is between 0.1 % and 25 %, preferably between 3 and 15 %.

10 The metallic element M is introduced into the zeolite by a cation exchange.

"Zeolite" is intended to mean a crystalline tectosilicate of natural or synthetic origin in which the crystals result from the three-dimensional assembly of tetrahedral  $\text{SiO}_4$  and  $\text{TO}_4$  units, T denoting a trivalent element such as aluminium, gallium, boron, and iron, preferably aluminium.

Zeolites of aluminosilicate type are the most common ones.

20 Within the crystal lattice zeolites have a system of cavities connected together by channels of a well-defined diameter, which are called pores.

Zeolites may have a one-dimensional, two-dimensional or three-dimensional network of channels.

25 A natural or synthetic zeolite may be used in the process of the invention.

Examples which may be mentioned of natural zeolites that can be employed are, for example: chabazite, clinoptilolite, erionite, phillipsite and

offretite.

Synthetic zeolites are wholly suitable for carrying out the invention.

Examples which may be mentioned of synthetic 5 zeolites with a one-dimensional network are, among others, zeolite ZSM-4, zeolite L, zeolite ZSM-12, zeolite ZSM-22, zeolite ZSM-23 and zeolite ZSM-48.

Examples which may be mentioned of zeolites with a two-dimensional network, which are preferably 10 employed, are zeolite  $\beta$ , mordenite and ferrierite.

Insofar as the zeolites with a three-dimensional network are concerned, zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZSM-11 and offretite may more particularly be mentioned .

15 Synthetic zeolites are preferably used and, more particularly, the zeolites which are in the following forms:

- mazzite with an Si/Al molar ratio of 3.4,
- zeolite L with an Si/Al molar ratio of 1.5
- 20 to 3.5,
- mordenite with an Si/Al molar ratio of 5 to 15,
- ferrierite with an Si/Al molar ratio of 3 to 10,
- 25 - offretite with an Si/Al molar ratio of 4 to 8.5,
- zeolites  $\beta$  with an Si/Al molar ratio higher than 8, preferably of between 10 and 35 and,

still more preferably, between 12 and 35,  
- zeolites Y, in particular the zeolites  
obtained after dealumination treatment (for  
example hydrotreatment, washing with  
hydrochloric acid or treatment with  $\text{SiCl}_4$ ),  
and it is possible to mention more  
particularly zeolites US-Y with an Si/Al  
molar ratio higher than 3, preferably between  
6 and 60,

10 - zeolite X of faujasite type with an Si/Al  
molar ratio of 0.7 to 1.5,  
- zeolites ZSM-5 or aluminium silicalite with  
an Si/Al molar ratio of 10 to 500,  
- zeolite ZSM-11 with an Si/Al molar ratio of  
15 5 to 30.

Among all these zeolites the zeolites  $\beta$  and Y  
are preferably used in the process of the invention.

The zeolites used in the process of the  
invention are known products described in the  
20 literature [cf. Atlas of zeolite structure types by  
W. M. Meier and D. H. Olson, published by the Structure  
Commission of the International Zeolite Association  
(1978)].

Commercially available zeolites may be used  
25 or else they may be synthesized according to the  
processes described in the literature.

Reference may be made to the abovementioned  
Atlas and, more particularly, for the preparation:

- of zeolite L, to the publication by  
R. M. Barrer et al., Z. Kristallogr., 128,  
pp. 352 (1969)
- 5 - of zeolite ZSM-12, to US Patent 3 832 449  
and the paper by LaPierre et al., Zeolites 5,  
pp. 346 (1985),
- of zeolite ZSM-22, to the publication by  
G. T. Kokotailo et al., Zeolites 5, pp. 349  
(1985),
- 10 - of zeolite ZSM-23, to US Patent 4 076 842  
and the paper by A. C. Rohrman et al.,  
Zeolites 5, pp. 352 (1985),
- of zeolite ZSM-48, to the work by  
J. L. Schlenker et al., Zeolites 5, pp. 355  
(1985),
- 15 - of zeolite  $\beta$ , to US Patent 3 308 069 and  
the paper by P. Caullet et al., Zeolites 12,  
pp. 240 (1992),
- of mordenite, to the work by  
Itabashi et al., Zeolites 6, pp. 30 (1986),
- 20 - of zeolites X and Y, to patents  
US 2 882 244 and US 3 130 007 respectively,
- of zeolite ZSM-5, to US Patent 3 702 886  
and the paper by V. P. Shiralkar et al.,  
Zeolites 9, pp. 363 (1989), and
- 25 - of zeolite ZSM-11, to the work by  
I. D. Harrison et al., Zeolites 7, pp. 21  
(1987).

Zeolites can be employed in various forms in  
the process of the invention: powder, shaped products  
such as granules (for example cylinders or beads),  
tablets and monoliths (honeycomb-shaped blocks), which  
5 are obtained by extrusion, moulding, compacting or any  
other known process type. In practice, on an industrial  
scale, it is the forms of granules, beads or monoliths  
that are the most advantageous ones, both from the  
viewpoint of effectiveness and the viewpoint of  
10 convenience in use.

The invention does not rule out the presence  
of binders employed during the forming of the zeolite,  
for example aluminas or clays.

Whichever the zeolite chosen, a treatment  
15 which makes it acidic is carried out if necessary.

Conventional treatments are used for this  
purpose.

Thus, the alkali metal cations can be  
exchanged by subjecting the zeolite to a treatment  
20 carried out with aqueous ammonia, thus resulting in an  
exchange of the alkali metal cation with an ammonium  
ion, and then the exchanged zeolite may be calcined in  
order to decompose the ammonium cation thermally and to  
replace it with an H<sup>+</sup> ion.

25 The quantity of aqueous ammonia to be used is  
at least equal to the quantity needed to exchange all  
the alkali metal cations for NH<sub>4</sub><sup>+</sup> ions.

From 10<sup>-5</sup> to 5 × 10<sup>-3</sup> mol of aqueous ammonia

therefore used per gram of zeolite.

The exchange reaction of the cation which can be exchanged with  $\text{NH}_4^+$  is performed at a temperature which lies between the ambient temperature and the 5 reflux temperature of the reaction medium. The operation takes a few hours and can be repeated.

The zeolite can also be acidified by being subjected to a conventional acid treatment. This treatment may be performed by adding an acid such as 10 especially hydrochloric acid, sulphuric acid, nitric acid, perchloric acid, phosphoric acid and trifluoromethanesulphonic acid.

According to a preferred embodiment the zeolite is acidified by the passage of a volume of acid 15 which has a normality between 0.1 and 2 N per gram of zeolite, of between 10 ml/g and 100 ml/g. This passage can be carried out in a single stage or, preferably, in a number of successive stages.

Conventional techniques, which are known 20 per se, for the preparation of supported metal catalysts can be used to prepare the catalysts involved in the process of the invention. For the preparation of the various catalysts reference may be made, in particular, to the work: J. F. Lepage "Catalyse de 25 contact", conception, préparation et mise en oeuvre des catalyseurs industriels ["Contact catalysis", design, preparation and use of industrial catalysts], Technip publishers (1978).

One method of preparation of the catalysts of the invention consists in depositing the element(s) M on the zeolite, precipitating the compounds in a manner known per se and subjecting the contact mass thus obtained to drying and a calcination.

Other methods of preparation are also possible, in particular one method of manufacture of the said catalysts consists in performing the impregnation of the zeolite with an impregnating solution including at least one appropriate compound of the chosen metallic elements, in a volatile solvent, preferably water, and then drying and calcining the contact mass thus obtained.

The zeolite may be chemically modified by impregnation by a dry or wet route.

Thus, one method of preparation consists in performing the dry impregnation of the zeolite with the aid of a solution of at least one compound of a metallic element of group 8.

The impregnation is carried out dry, that is to say that the total volume of solution employed is approximately equal to the total pore volume exhibited by the zeolite. The product obtained is dried and calcined.

More precisely, the dry impregnation consists in adding to a mass  $m_1$  of a powdered product to be impregnated a volume V of an aqueous solution of one or more salts of cations or of anions to be bound onto the

surface of the solid. The solution volume  $V$  is chosen such that  $V/m_1$  is equal to the water pore volume of the solid to be impregnated.

The concentration  $C$  of cations or anions of  
5 the impregnating solution is chosen such that the ratio  $CVM_2/m_1$  is equal to the chosen weight percentage of impregnating species bound onto the surface of the product to be impregnated (with  $M_2$  = molecular mass of the impregnating species). The solution is added  
10 dropwise so as to obtain a homogeneous adsorption.

The product can then be left to stand for a variable period at ambient temperature. The product is then dried according to conventional techniques which are known to a person skilled in the art. The drying is  
15 generally conducted at atmospheric pressure or at reduced pressure or by freeze-drying. It may also be calcined.

The wet-route impregnation is done by dispersing the zeolite in an aqueous solution of salts  
20 of cations and/or anions to be bound onto the surface of the solid.

This solution may have a concentration of the impregnating species which varies from  $10^{-3}$  M to 10 M.

The pH of the solution may be advantageously  
25 adjusted to a value that is at least equal to that of the isoelectric point of the product to be modified in order to bind the cations preferentially (usual case); however, this condition is not essential. Below this

isoelectric point it is possible to bind the cations correctly when the associated anions are highly "covalent" in character.

The solution temperature may vary from the  
5 ambient to 100°C.

The dispersion is stirred vigorously for a variable time.

The product is then filtered off and optionally washed.

10 According to both alternative forms as described above a zeolite is obtained on which at least one metallic element M is deposited.

15 The deposition of several metallic elements on the zeolite can, of course, be carried out successively but, preferably, simultaneously.

In the following stages the modified zeolite is subjected to a drying operation conducted advantageously at a temperature varying from 50°C to 200°C for a period ranging preferably from 2 to  
20 12 hours.

25 Insofar as the calcination operation is concerned, this is conducted at a temperature of between 200°C and 700°C, preferably between 400°C and 600°C for a period varying from 1 to 15 hours, preferably from 2 to 6 hours.

The nature of the compounds supplying the various elements employed for the preparation of the catalysts of the invention is not critical.

The metallic elements M may be supplied in the form of a metal or in the form of an inorganic derivative such as an oxide or a hydroxide. Use may be made of an inorganic salt, preferably nitrate,

5 sulphate, oxysulphate, halide, oxyhalide, silicate or carbonate, or an organic derivative, preferably cyanide, oxalate or acetylacetone, alcoholate and still more preferably methylate or ethylate, carboxylate and still more preferably acetate.

10 Complexes may also be used, especially chlorinated or cyanated ones of metals M and/or of alkali metals, preferably sodium or potassium or of ammonium.

Examples of compounds capable of being used for the preparation of the catalysts of the invention which may be mentioned are especially:

- in the case of iron:

iron(II) bromide  
iron(III) bromide  
anhydrous or hydrated iron(II) chloride  
20 anhydrous or hydrated iron(III) chloride  
iron(II) iodide  
iron(III) iodide  
iron(II) fluoride  
iron(III) fluoride  
25 iron(II) hydroxide  
anhydrous or hydrated iron(II) carbonate  
iron(II) nitrate  
iron(III) nitrate

anhydrous or hydrated iron(II) sulphate  
anhydrous or hydrated iron(III) sulphate  
iron(III) hydroxysulphate  
anhydrous or hydrated iron(II) oxide  
5 anhydrous or hydrated iron(III) oxide  
iron(II) orthophosphate  
iron(III) orthophosphate  
iron(III) oxalate  
iron(II) acetate  
10 basic iron(III) acetate  
iron(II) citrate  
iron(III) citrate  
iron(III) acetylacetone  
iron(II) hexamine chloride  
15 - in the case of nickel:  
nickel(II) bromide  
nickel(II) chloride  
nickel(II) iodide  
nickel(II) carbonate  
20 basic nickel(II) carbonate  
nickel(II) cyanide  
hydrated nickel(II) nitrate  
anhydrous or hydrated nickel(II) sulphate  
nickel(II) oxide  
25 nickel(II) hydroxide  
nickel(II) acetate  
nickel(II) tetramine nitrate  
nickel(II) hexamine nitrate

nickel(II) tetramine chloride

nickel(II) hexamine chloride

- in the case of ruthenium:

ruthenium(III) chloride

5           ruthenium(IV) chloride

rutheniumpentrafluoride

ruthenium(III) hydroxide

ruthenium(II) oxide

ruthenium(IV) oxide

10           ruthenium oxychloride treated with aqueous ammonia ,

$\text{Ru}_2(\text{OH})_2\text{Cl}_4 \cdot 7\text{NH}_3 \cdot 5\text{H}_2\text{O}$

ruthenium acetate

- in the case of palladium:

palladium(II) bromide

15           palladium(II) chloride

palladium(II) iodide

palladium(II) cyanide

hydrated palladium(II) nitrate

dihydrated palladium(II) sulphate

20           palladium(II) monoxide, hydrated or otherwise

palladium(IV) dioxide, hydrated or otherwise

palladium(II) acetate

palladium(II) acetylacetonate

ammonium tetrachloropalladate(II)

25           potassium hexachloropalladate(IV)

palladium(II) tetramine nitrate

palladium(II) dichlorobis(acetonitrile)

palladium(II) dichlorobis(benzonitrile)

palladium(II) dichloro(1,5-cyclooctadiene)  
palladium(II) dichlorodiamine  
- in the case of platinum:  
platinum(II) bromide  
5 platinum(II) chloride  
platinum(IV) chloride  
platinum(II) iodide  
platinum(II) hydroxide  
hydrated platinum(II) hydroxide  
10 platinum(II) monoxide, hydrated or otherwise  
platinum(IV) dioxide, hydrated or otherwise  
platinum(II) cyanide  
platinum(II) acetylacetonate  
potassiumbis(oxalato)platinate(II)  
15 ammonium tetrachloroplatinate(II)  
ammonium hexachloroplatinate(IV)  
hydrated sodium tetrachloroplatinate(IV)  
hexahydrated sodium hexachloroplatinate(IV)  
potassium hexachloroplatinate(IV)  
20 potassium hexacyanoplatinate(IV)  
hydrated platinum(II) tetramine chloride  
hydrated platinum(II) tetramine hydroxide  
platinum(II) dichlorodiamine  
platinum(IV) tetrachlorodiamine  
25 platinum(II) dibromo(1,5-cyclooctadiene)  
platinum(II) dichloro(1,5-cyclooctadiene)  
platinum(II) dichlorobis(benzonitrile)  
platinum(II) dichlorobis(pyridine)

hexahydrated chloroplatinic acid

platinum(II) bis(ethylenediamine) chloride

- in the case of rhodium:

rhodium(III) bromide

5 anhydrous rhodium(III) chloride

hydrated rhodium(III) chloride

rhodium(III) iodide

rhodium(III) nitrate

rhodium(IV) dioxide, hydrated or otherwise

10 rhodium(III) sesquioxide, hydrated or otherwise

rhodium(II) acetate dimer

rhodium(III) acetylacetonate

hydrated sodium hexachlororhodate(III)

ammonium hexachlororhodate(III)

15 rhodium(I) acetylacetonatobis(ethylene)

potassium hexanitritorhodate(III)

- in the case of osmium:

osmium(II) chloride

osmium(III) chloride

20 osmium(IV) chloride

osmium(IV) iodide

osmium(II) oxide

osmium(III) oxide

osmium(IV) oxide

25 - in the case of iridium:

iridium(III) bromide

iridium(IV) bromide

iridium(II) chloride

iridium(III) chloride  
iridium(IV) chloride  
iridium(III) iodide  
iridium(IV) iodide  
5 hydrated iridium(II) nitrate  
hydrated iridium(III) sulphate  
iridium(IV) dioxide, hydrated or otherwise  
irridium(III) sesquioxide, hydrated or otherwise  
iridium(II) acetate  
10 iridium(III) hexamine nitrate  
iridium(III) hexamine chloride

The catalyst obtained, consisting therefore  
of a zeolite which is modified and used as acylation  
catalyst, is very easily regenerated at the end of  
15 reaction.

An "acylation reaction" is intended to mean a  
reaction that is well known to a person skilled in the  
art, which consists in reacting a preferably aromatic  
substrate with an acylating agent, it being possible  
20 for the reaction to be conducted in vapour or liquid  
phase.

After removal of the liquid phase if  
necessary, a hot gaseous stream of molecular oxygen or  
of a gas containing it is directed onto the catalyst.

25 This gas may be pure oxygen or oxygen diluted  
with an inert gas, for example nitrogen, or a rare gas,  
for example argon. Air is preferably used.

The gas flow rate is, for example, from 0.1

to 50 litres/hour.

The temperature of the gas flow is advantageously lower than 350°C and is preferably between 100°C and 250°C.

5 The duration of the treatment may vary widely, for example between 1 and 20 hours.

At the end of reaction a catalyst is recovered which has regained all of its initial catalytic activity.

10 It is therefore noted that the regeneration is performed at low temperature, in contrast to what is usually done with a simple zeolite.

An illustration of the regeneration of a modified zeolite-based catalyst is given in the 15 acylation reaction of an aromatic ether, which follows.

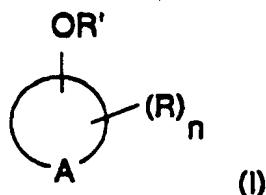
Furthermore, it was found that the zeolite doped with an element of the platinum group was a very good catalyst for the reaction of acylation of an aromatic ether.

20 Another subject of the present invention is a process for acylation of an aromatic ether, which consists in reacting the said aromatic ether with an acylating agent, in the presence of a catalyst, and then in recovering the product formed, the said process 25 being characterized in that the acylation reaction is conducted in the presence of an effective quantity of a zeolite modified with at least one element M<sub>1</sub> of the platinum group.

According to a preferred alternative form of the process of the invention the acylation of the aromatic ether is performed first of all by reacting it with an acylating agent, in the presence of a zeolite 5 modified with a metallic element M<sub>1</sub> as defined and then, after reaction, the regeneration of the catalyst is carried out by heat-treating the said zeolite with a gas containing molecular oxygen.

In the following description of the present 10 invention "aromatic ether" is intended to mean an aromatic compound in which a hydrogen atom bonded directly to the aromatic nucleus is replaced with an ether group and "aromatic compound" the conventional concept of aromaticity, as defined in the literature, 15 especially by Jerry March, Advanced Organic Chemistry, 4th edition, John Wiley and Sons, 1992, pp. 40 et seq.

More precisely, the subject of the present invention is a process for acylation of an aromatic ether of general formula (I):



20 in which:

- A symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic aromatic carbocyclic system, the system including at least one OR' group, it being possible for the said cyclic residue to carry one

or more substituents,

- R denotes one or several identical or different substituents,
- R' denotes a hydrocarbon radical containing from 1 to 24 carbon atoms, which may be a linear or branched, saturated or unsaturated, acyclic aliphatic radical, a saturated or unsaturated cycloaliphatic or monocyclic or polycyclic aromatic radical, or a linear or branched, saturated or unsaturated, aliphatic radical, carrying a cyclic substituent,
- n is a number smaller than or equal to 4.

In the present text "alkoxy groups" is used, in a simplified manner, to denote the groups of the R'-O- type in which R' has the meaning given above. R' therefore denotes equally well a saturated or unsaturated acyclic aliphatic or cycloaliphatic or aromatic radical or a saturated or unsaturated aliphatic radical carrying a cyclic substituent.

The aromatic ether which is involved in the process of the invention corresponds to the formula (I) in which R' denotes a linear or branched, saturated or unsaturated, acyclic aliphatic radical.

More preferably R' denotes a linear or branched alkyl radical containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, it being optionally possible for the hydrocarbon chain to be interrupted by a heteroatom (for example oxygen) or by a functional group (for example -CO-) and/or to carry a

substituent (for example a halogen or a carboxylic group).

The linear or branched, saturated or unsaturated, acyclic aliphatic radical may optionally 5 carry a cyclic substituent. A ring is intended preferably to mean a saturated, unsaturated or aromatic carbocyclic ring, preferably cycloaliphatic or aromatic, especially cycloaliphatic containing 6 carbon atoms in the ring, or a benzene ring.

10 The acyclic aliphatic radical may be linked to the ring by a valency bond, a heteroatom or a functional group, and examples are given below.

15 The ring may be optionally substituted and, by way of examples of cyclic substituents, it is possible to envisage, among others, substituents such as R, the meaning of which is specified in the case of formula (Ia).

R' may also denote a carbocyclic radical which is saturated or includes 1 or 2 unsaturations in 20 the ring, generally containing from 3 to 8 carbon atoms, preferably 6 carbon atoms, in the ring, it being possible for the said ring to be substituted with substituents such as R.

25 R' may also denote an aromatic, preferably monocyclic, carbocyclic radical generally containing at least 4 carbon atoms, preferably 6 carbon atoms, in the ring, it being possible for the said ring to be substituted with substituents such as R.

The process of the invention applies very particularly to the aromatic ethers of formula (I) in which R' denotes a linear or branched alkyl radical containing from 1 to 4 carbon atoms or a phenyl radical.

Examples of preferred radicals R' according to the invention which may be mentioned are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl and phenyl radicals.

In the general formula (I) of the aromatic ethers the residue A may denote the residue of a monocyclic aromatic carbocyclic compound containing at least 4 carbon atoms and preferably 6 carbon atoms or the residue of a polycyclic carbocyclic compound which may consist of at least 2 carbon rings which are aromatic and which form ortho- or ortho- and pericondensed systems between them or of at least 2 carbon rings of which at least one is aromatic, and which form ortho- or ortho- and pericondensed systems between them.

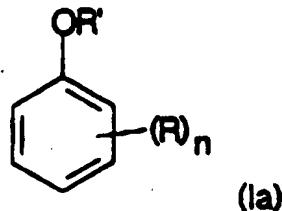
The residue A may carry one or more substituents on the aromatic nucleus.

Examples of substituents R are given below, but this list is not limiting in character. Any substituent whatever may be present on the ring, provided that it does not interfere with the desired product.

Since the residue A can, among other things,

carry several alkoxy groups, it is possible to acylate polyalkoxylated compounds according to the process of the invention.

The process of the invention applies more 5 particularly to the aromatic ethers of formula (Ia):



in which:

- n is a number smaller than or equal to 4, preferably equal to 0, 1 or 2,
- the radical R' denotes a linear or branched alkyl radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl or phenyl,
- the radical(s) R denote one of the following atoms or groups:

  - a hydrogen atom,
  - a linear or branched alkyl radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl,
  - a linear or branched alkoxy radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy,

isopropoxy, butoxy, isobutoxy, sec-butoxy or  
tert-butoxy radicals,

- a halogen atom, preferably a fluorine, chlorine  
or bromine atom, or a trifluoromethyl radical,

5 - the radicals R' and R and the 2 successive atoms of  
the benzene ring can together form a ring containing  
from 5 to 7 atoms, optionally including another  
heteroatom.

When n is greater than or equal to 1 the  
10 radicals R' and R and the 2 successive atoms of the  
benzene ring may be linked together by an alkylene,  
alkenylene or alkenylidene radical containing from 2 to  
4 carbon atoms, to form a saturated, unsaturated or  
aromatic heterocyclic ring containing from 5 to 7  
15 carbon atoms. One or more carbon atoms may be replaced  
by another heteroatom, preferably oxygen. The radicals  
R' and R can thus denote a methylenedioxy or  
ethylenedioxy radical.

The process of the invention applies more  
20 particularly to the aromatic ethers of formula (Ia) in  
which n is equal to 1, the radicals R and R' both  
denoting identical or different alkoxy radicals.

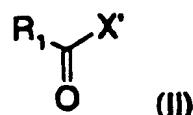
By way of illustration of compounds  
corresponding to the formula (I) there may be mentioned  
25 more particularly:

- monoethers such as anisole, ethoxybenzene  
(phenetole), butoxybenzene, isobutoxybenzene,  
2-chloroanisole, 3-chloroanisole, 2-bromoanisole,

3-bromoanisole, 2-methylanisole, 3-methylanisole,  
 2-ethylanisole, 3-ethylanisole, 2-isopropylanisole,  
 3-isopropylanisole, 2-propylanisole, 3-propylanisole,  
 2-allylanisole, 2-butyranisole, 3-butyranisole,  
 5 2-benzylanisole, 2-cyclohexylanisole, 1-bromo-2-  
 ethoxybenzene, 1-bromo-3-ethoxybenzene, 1-chloro-2-  
 ethoxybenzene, 1-chloro-3-ethoxybenzene, 1-ethoxy-2-  
 ethylbenzene, 1-ethoxy-3-ethylbenzene, 2,3-dimethyl-  
 anisole and 2,5-dimethylanisole,  
 10 - diethers such as veratrole, 1,3-dimethoxybenzene,  
 1,2-diethoxybenzene, 1,3-diethoxybenzene,  
 1,2-dipropoxybenzene, 1,3-dipropoxybenzene,  
 1,2-methylenedioxybenzene and 1,2-ethylenedioxybenzene,  
 - triethers such as 1,2,3-trimethoxybenzene,  
 15 1,3,5-trimethoxybenzene and 1,3,5-triethoxybenzene.

The compounds to which the process according  
 to the invention applies in a more particularly  
 advantageous manner are anisole and veratrole.

With regard to the acylating reactant, this  
 20 corresponds more particularly to the formula (II):



in which:

-  $R_1$  denotes:  
 - a linear or branched, saturated or unsaturated,  
 aliphatic radical containing from 1 to 24 carbon  
 25 atoms, a saturated, unsaturated cycloaliphatic or

monocyclic or polycyclic aromatic radical containing from 3 to 8 carbon atoms, or a linear or branched, saturated or unsaturated, aliphatic radical carrying a cyclic substituent,

5 - X' denotes:

- a halogen atom, preferably a chlorine or bromine atom,
- a hydroxyl group,
- a radical -O-CO-R<sub>2</sub> with R<sub>2</sub>, identical or

10 different from R<sub>1</sub>, having the same meaning as R<sub>1</sub>, it being possible for R<sub>1</sub> and R<sub>2</sub> to form together a linear or branched, saturated or unsaturated aliphatic divalent radical containing at least 2 carbon atoms.

15 By cyclic substituent reference is made to what is described above.

More preferably R<sub>1</sub> denotes a linear or branched alkyl radical containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, it being 20 possible for the hydrocarbon chain to be optionally interrupted by a heteroatom (for example oxygen), by a functional group (for example -CO-) and/or to carry a substituent (for example a halogen or a CF<sub>3</sub> group).

R<sub>1</sub> preferably denotes an alkyl radical containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl.

The radical R<sub>1</sub> also denotes preferably a

phenyl radical which may be optionally substituted. Any substituent whatever may be present on the ring, provided that it does not interfere with the desired product.

5           More particular examples of substituents which may be mentioned are, especially:

- a linear or branched alkyl radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl,

10          isopropyl, butyl, isobutyl, sec-butyl or tert-butyl,

- a linear or branched alkoxy radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as the methoxy, ethoxy,

15          propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy and tert-butoxy radicals,

- a hydroxyl group,

- a halogen atom, preferably a fluorine, chlorine or bromine atom.

20          The preferred acylating agents are acid anhydrides. They correspond more particularly to the formula (II) in which R<sub>1</sub> and R<sub>2</sub> are identical and denote an alkyl radical containing from 1 to 4 carbon atoms.

When the acylating agent is an acid halide, 25 it corresponds preferably to the formula (II) in which X' denotes a chlorine atom and R<sub>1</sub> denotes a methyl or ethyl radical.

By way of illustration of acylating agents

corresponding to the formula (II) there may be mentioned more particularly:

- acetic anhydride,
- propanoic anhydride,
- 5 - isobutyric anhydride,
- trifluoroacetic anhydride,
- benzoic anhydride,
- acetyl chloride,
- monochloroacetyl chloride,
- 10 - dichloroacetyl chloride,
- propanoyl chloride,
- isobutanoyl chloride,
- pivaloyl chloride,
- stearoyl chloride,
- 15 - crotonyl chloride,
- benzoyl chloride,
- chlorobenzoyl chlorides,
- p-nitrobenzoyl chloride,
- methoxybenzoyl chlorides,
- 20 - naphthoyl chlorides,
- acetic acid.

In accordance with the invention the acylation reaction is advantageously conducted in liquid phase including the aromatic ether and the 25 acylating agent, in the presence of the catalyst.

One of the starting reactants may be used as reaction solvent, but it is also possible to use an organic solvent.

As examples of solvents which are suitable for the present invention there may be mentioned in particular aliphatic or aromatic hydrocarbons, halogenated or otherwise, and aliphatic, cycloaliphatic 5 or aromatic ethers.

Examples of aliphatic hydrocarbons which may be mentioned more particularly are the paraffins such as especially hexane, heptane, octane, nonane, decane, undecane, dodecane, tetradecane or cyclohexane and 10 naphthalene and the aromatic hydrocarbons and more particularly the aromatic hydrocarbons like especially benzene, toluene, xylenes, cumene and the petroleum cuts consisting of a mixture of alkylbenzenes, especially the cuts of Solvesso® type.

15 Insofar as the aliphatic or aromatic halogenated hydrocarbons are concerned, it is possible to mention more particularly the perchlorinated hydrocarbons such as especially tetrachloroethylene and hexachloroethane, partially chlorinated hydrocarbons 20 such as dichloromethane, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, trichloroethylene, 1-chlorobutane and 1,2-dichlorobutane, monochlorobenzene, 25 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene or mixtures of various chlorobenzenes, bromoform, bromoethane or 1,2-dibromoethane, monobromobenzene or mixtures of

monobromobenzene with one or more dibromobenzenes, and 1-bromonaphthalene.

Aliphatic, cycloaliphatic or aromatic ethers may also be employed as organic solvents and, more particularly, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, methyl tert-butyl ether, dipentyl ether, diisopentyl ether, ethylene glycol dimethyl ether (or 1,2-dimethoxyethane), diethylene glycol dimethyl ether (or 1,5-dimethoxy-3-oxapentane), benzyl ether, dioxane and tetrahydrofuran (THF).

Use may be made of polar aprotic solvents such as the nitro compounds like, for example, nitromethane, nitroethane, 1-nitropropane, 15 2-nitropropane or mixtures thereof, nitrobenzene, aliphatic or aromatic nitriles like acetonitrile, propionitrile, butanenitrile, isobutanenitrile, benzonitrile and benzyl cyanide, and tetramethylene sulphone (sulpholane).

20 The preferred solvents are dichloromethane, tetrachloromethane, THF and diethyl ether.

A mixture of organic solvents may also be employed.

The starting substrate is preferably employed 25 as reaction solvent.

In a first stage of the process of the invention the acylation of the aromatic ether is conducted. According to a preferred alternative form

the regeneration of the catalyst is performed in a following stage.

The ratio of the number of moles of aromatic ether to the number of moles of acylating agent may 5 vary because the substrate may be used as reaction solvent. The ratio may thus range from 0.1 to 10 and preferably lies between 0.5 and 4.0.

The quantity of catalyst which is used in the process of the invention may vary within wide limits.

10 When the process is carried out noncontinuously, the catalyst may represent from 0.01 to 50 %, preferably from 1.0 to 20 %, by weight relative to the aromatic ether introduced.

However, if the process is carried out 15 continuously, for example by reacting a mixture of the aromatic ether and of the acylating agent on a stationary catalyst bed, these catalyst/aromatic ether ratios are meaningless and, at a given instant there may be a weight excess of catalyst in relation to the 20 starting aromatic ether. In this case the residence time of the flow of material over the catalyst bed varies, for example, between 5 min and 10 hours and preferably between 15 min and 3 hours, depending on the reaction temperature and the desired degree of 25 conversion.

With regard to the quantity of organic solvent which is used, this is generally chosen so that the ratio of the number of moles of organic solvent to

the number of moles of aromatic ether varies preferably between 0 and 100 and still more preferably between 0 and 50.

The temperature at which the acylation reaction is carried out depends on the reactivity of the starting substrate and that of the acylating agent.

It lies between 20°C and 300°C, preferably between 40°C and 200°C.

The reaction is generally conducted at atmospheric pressure, but lower or higher pressures may also be suitable. The work is done at autogenous pressure when the reaction temperature is higher than the boiling temperature of the reactants and/or of the products.

From a practical viewpoint the process may be operated noncontinuously or continuously.

According to the first alternative form there are no constraints concerning the use of the reactants. They may be introduced in any order.

After the reactants have been brought into contact the reaction mixture is heated to the desired temperature.

The other alternative form of the invention consists in conducting the reaction continuously, in a tubular reactor comprising the solid catalyst placed in a stationary bed.

The aromatic ether and the acylating agent may be introduced into the reactor separately or as a

mixture.

They may also be introduced in a solvent such as mentioned above.

At the end of reaction a liquid phase is recovered including the acylated aromatic ether, which may be recovered in a conventional way, by distillation or by recrystallization from a suitable solvent, after preliminary removal of the excess reactants.

According to a preferred embodiment of the invention a regeneration of the catalyst employed is performed in a following stage of the process of the invention.

After removal of the liquid phase a hot gaseous stream of molecular oxygen or of a gas containing it is sent over the catalyst.

The regeneration of the catalyst is conducted as described above.

At the end of treatment a catalyst is recovered which has regained all its initial catalytic activity.

The process of the invention is particularly well suited to the preparation of 4-methoxyacetophenone and of 3,4-dimethoxyacetophenone, commonly called acetoveratrole, by acetylation of anisole or of veratrole respectively.

An advantage of the process of the invention is that the acylation reaction takes place without there being any O-dealkylation of the starting aromatic

ether.

In addition, the presence of little ortho isomer is observed, because of the para-orienting nature of the catalyst.

5 The examples which follow illustrate the invention without, however, limiting it.

In the examples the yields mentioned correspond to the following definition:

Yield:  $RY_{A.A.} = \frac{\text{number of moles of acylating agent which are introduced}}{\text{number of moles of acylated aromatic compound which are formed}} \times 100\%$

Example 1

Preparation of a zeolite  $\beta$  modified with palladium.

The following are placed in a 250-cm<sup>3</sup> polyethylene bottle:

- 39.5 cm<sup>3</sup> of a solution of palladium tetrammine hydroxide  $Pd(NH_3)_4(OH)_2$ ; solution CLAL 8949 containing 15.2 g/l of palladium,
- 60.5 cm<sup>3</sup> of deionized water.

20 20 g of a powdered zeolite  $\beta$  in H<sup>+</sup> form, marketed by Valdor under the name (PQ)CBV 811-25 are added next.

The materials are agitated for 24 h at ambient temperature (20°C).

25 The modified zeolite is separated off by centrifuging, is dried in the oven at 110°C and is then calcined at 450°C for 2 hours.

A zeolite containing 3 % by weight of

palladium is obtained.

Example 2

13 ml of zeolite Pd (3 %)/H $\beta$  (i.e. approximately 5 g) in the form of powder prepared 5 according to Example 1 are introduced into a tubular reactor heated by a jacket.

The jacket is heated to 100°C and a mixture of anisole and of acetic anhydride, used in a molar ratio of 2, is then introduced through the bottom of 10 the reactor with the aid of an HPLC pump, at a flow rate of 0.2 ml/min.

The reaction mixture is drawn off continuously by overflowing.

The reaction yield is followed in the course 15 of time by removing aliquots which are then analysed by vapour phase chromatography.

After 100 hours' reaction the acetonitrile yield has dropped to approximately 10 %.

Table (I): initial activity

Time (h)	Yield (%/acetic anhydride)
3.5	72
7.5	73
30	50
51.2	26.2
70	20
94.3	13
100	10

The reactor is drained and the catalyst is reactivated in air at 190°C for 3 hours.

The injection of the anisole/acetic anhydride mixture (2/1) at 100°C is then restarted.

5 The following performance is obtained:

Table (II): after reactivation (in air,  
3 h at 190°C)

Time (h)	Yield (%/acetic anhydride)
2.6	73.2
11	58
36	34.5
51	24
70	20
93	13

15 Example 3

13 ml of zeolite Pd (3 %)/H $\beta$  (i.e. approximately 5 g) prepared according to Example 1, in the form of extrudates containing 40 % of alumina binder, are introduced into a tubular reactor heated by 20 a jacket.

The jacket is heated to 105°C and a mixture of anisole and of acetic anhydride used in a molar ratio of 2 is then introduced through the bottom of the reactor with the aid of an HPLC pump, at a flow rate of 25 0.2 ml/min.

The reaction mixture is drawn off continuously by overflow.

The yield of the reaction is followed in the

course of time by removing aliquots which are then analysed by vapour phase chromatography.

After 120 hours' reaction the yield of acetoanisole has dropped to approximately 13 %.

5

Table (III): initial activity

10

Time (h)	Yield (%/acetic anhydride)
4	70
5	75
30	40
53	29
70	24.7
100	23.2
120	13.4

15

The reactor is drained and the catalyst is reactivated in air at 180°C for 3 hours.

The injection of the anisole/acetic anhydride (2/1) mixture at 105°C is then restarted.

20

Table (IV): after reactivation (in air,  
3 h at 180°C

25

Time (h)	Yield (%/acetic anhydride)
4.3	53
6	56
21.2	32.5
23.3	31.4